RICE HUSK ASH SILICA AS A SUPPORT MATERIAL FOR IRON AND RUTHENIUM BASED HETEROGENEOUS CATALYST

by

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WITH LOVE

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TABLE OF CONTENTS

CHAPTER 3 - SAMPLE CHARACTERIZATION

CHAPTER 4 - CATALYTIC ACTIVITY

CHAPTER 5 - CONCLUSION

List of Abbreviation

XRD	– X-ray Diffractometry
BET	– Brunauer-Emmett-Teller
SEM	–Scanning Electron Microscopy
EDX	– Energy dispersive Spectrometry
FTIR	– Fourier Transform Infra-Red
RHA	– Rice Husk Ash
RHA-Fe	– Iron incorporated Rice Husk Ash
RHA-Fe 700	– Iron incorporated Rice Husk Ash calcined at 700 ºC
RHA-Ru	– Ruthenium incorporated Rice Husk Ash
RHA- Ru 700	– Ruthenium incorporated Rice Husk Ash calcined at 700 ºC
LOI	– Loss of Ignition
TGA	– Thermal Gravimetric Analysis
GC-MS	– Gas Chromatography- Mass Spectra
NR	– Natural Rubber
LLDPE	– Linear Low Density Polyethylene
FRP	– Fiber-reinforced Plastic
HPA	– Heteroply Acid
ODH	– Oxidative dehydrogenation
TOF	– Turn over frequency

List of Table

List of Figures

List of Schemes

ABU SEKAM PADI – BAHAN PENYOKONG BAGI MANGKIN OKSIDA LOGAM (FERUM DAN RUTHENIUM) HETEROGEN

ABSTRAK

Sampel silika daripada abu sekam padi yang disokong oleh logam ferum dan ruthenium telah disediakan melalui teknik sol-gel. Ia disediakan dengan larutan akues garam logam dan HNO_3 3.0 M. Analisis XRD menunjukkan bahawa kesemua sampel yang telah disediakan itu wujud dalam keadaan amorfus. Nilai BET bagi RHA-Fe dan RHA-Fe 700 didapati adalah 87.40 dan 55.83 $m^2\,g^{-1}$. RHA-Fe dan RHA-Fe 700 bertindak aktif sebagai mangkin heterogen dalam tindak balas diantara toluene dan benzil klorida. Benzil klorida mono tertukarganti, didapati menjadi hasil utama tindakbalas ini dengan yield sebanyak 92%. GC pula menunjukkan kedua-dua isomer *ortho* dan *para* wujud pada kuantiti yang seakan sama. Sementara itu, dalam sampel silika dimana Ruthenium digunakan sebagai bahan penyokong, (RHA-Ru 700) telah menunjukkan sifai-sifat yang unik berbanding sampel RHA-Fe dan RHA-Fe 700. Gambarajah SEM bagi RHA-Ru700 yang wujud dalam keadaan amorfus, jelas menunjukkan pembentukkan nano rod yang permukaan luarannya rata. RHA-Ru mempunyai luas permukaan sebnyak ca. 65 $m^2\,g^{-1}$, sementara RHA-Ru 700 hanya menunjukkan nilai sebanyak 10 $m^2\,g^{-1}$. Penurunan pada nilai luas

permukaan adalah konsisten dengan pembentukkan rod yang berbentuk kristal. Mengikut graf taburan liang, terdapat dua taburan liang utama bagi RHA-Ru, yang masing-masing menunjukkan, diantara 40 dan 100 Å dan juga diantara 150 hingga 400 Å. Kesemua katalisis yang disediakan wujud dalam kedaan mesoporus.

RICE HUSK ASH SILICA AS A SUPPORT MATERIAL FOR IRON AND RUTHENIUM BASED HETEROGENEOUS CATALYST

ABSTRACT

Rice husk ash silica as a support material for iron (RHA-Fe) and ruthenium (RHA-Ru) based heterogeneous catalysts were prepared through the sol-gel technique using an aqueous solution of metal salt in 3.0 M HNO_3. The XRD analysis showed that all samples prepared were in amorphous state. The BET values for the RHA-Fe and RHA-Fe 700 (after calcinations) were found to be 87.40 and 55.83 $m^2 g^{-1}$ respectively. The prepared RHA-Fe and RHA-Fe700 were found to be active as heterogeneous catalysts and showed high activity in the reaction between toluene and benzyl chloride. The mono substituted benzyltoluene was the major product and both catalysts yielded more than 92% of this isomer. The GC shows that both the ortho and para substituted mono isomers were present in about equal quantities. The ruthenium derivates, RHA-Ru 700 showed very unique properties compared to the RHA-Fe samples. The SEM micrographs of RHA-Ru 700 showed the formation of well-defined flat elongated nano-sized rods with a smooth outer surface among the amorphous powder. RHA-Ru had a specific surface area of ca. 65 m^2 g^{-1}, while RHA-Ru 700 had only ca. 10 m^2 g^{-1}. The decrease in specific surface area was

consistent with the formation of the rod shaped crystalline phase. From the pore distribution graphs, there were two distinct pore size distributions for RHA-Ru. These were between 40 and 100 Å and between 150 to 400 Å respectively. All the catalysts prepared were shown to be mesoporous except for RHA-Ru 700 which shows some crystalline state after calcination.

List of publications made based on this project.

1. SILICA SUPPORTED METAL OXIDE CATALYST FROM RICE HUSK ASH

   Farook Adam, Bahruddin Saad, **Saraswathy Balakrishnan** and Fazliawati Mahayuddin *"Paper presented for the Regional Conference for Young Chemist 2004"*

2. SYNTHESIS AND CHARACTERISATION OF A NOVEL HETEROGENEOUS CATALYST FROM RICE HUSK ASH – THE FRIEDEL-CRAFT BENZYLATION OF TOLUENE WITH BENZYL CHLORIDE

   Farook Adam, Kalaivani Kandasamy and **Saraswathy Balakrishnan** *"Paper presented for the Regional Conference for Young Chemist 2004"*

3. SYNTHESIS AND CHARACTERISATION OF A NOVEL HETEROGENEOUS CATALYST FROM RICE HUSK ASH – THE FRIEDEL-CRAFT BENZYLATION OF TOLUENE WITH BENZYL CHLORIDE

   School of Chemical Sciences, Universiti Sains Malaysia. 11800 Penang, Malaysia.

*F.Adam, **B.Saraswathy,** K.Kalaivani, J. Colloid Interface Sci. 304 (2004) 137*

4. RICE HUSK ASH SILICA AS A NEW SUPPORT MATERIAL FOR RUTHENIUM BASED HETEROGENOUS CATALYST

   School of Chemical Sciences, Universiti Sains Malaysia. 11800 Penang, Malaysia.

   *F.Adam, **B.Saraswathy**, P.L Wong, Journal of Physical Science Vol. 17(2) 1-13, 2006*

5. RICE HUSK ASH – A SUPPORT FOR HETEROGENOUS METAL OXIDE CATALYSTS

   Saraswathy Balakrishnan. *School of Chemical Sciences, Universiti Sains Malaysia. 11800 Penang, Malaysia*

   Poster presentation during Post graduate week, 2004 organized by Institute of Post Graduate Studies, *Universiti Sains Malaysia. 11800 Penang, Malaysia*

CHAPTER ONE

LITERATURE REVIEW

1.0 INTRODUCTION

This review describes the usage of silica powders and gels in many industrial sectors and chemical reactions. This review will make an attempt to collect together data on all the research which has been carried out using rice husk ash as the main source of silica based products. Rice husk ash contains over 90% silica and can be an economically viable raw material for the production of silicates and silica. It has unique properties which makes it a valuable raw material with many uses.

Another interesting area is the supported metal catalysts on silica which are widely applied in many important reactions. Amorphous silica is well-known and commonly used as support material due to its high surface area where it will provide sufficient surface area for the metal to disperse. This review will also describe the methods involved in the preparation of such modified catalysts and its application in many chemical reactions.

1.1 RICE HUSK ASH

1.1.1 The source of Rice Husk Ash

South and South East Asia account for over 90 % of world's rice production. Like most other biomass material, rice husk contains a high amount of organic volatiles. Thus, rice husk is recognized as a potential source of energy. Moreover, its ~ 20 % ash content comprising of over 95 % amorphous silica would make the rice husk ash utilization economically attractive [1]. Rice husk is a milling by-product of rice and is a major waste product of the agriculture industry. It is also abundantly available. Rice husk is a residue produced in significant quantity on a global basis. While they are used as a fuel in some regions, in other countries they are treated as waste, causing pollution and disposal problems. Due to growing environmental concern, and the need to conserve energy and resources, efforts have been made to burn the husks under controlled conditions and to utilize the resultant ash as building material [2].

Rice husk ash (RHA) contains high amount of silicon dioxide. The non-crystalline phase in RHA obtained from combustion at temperatures below 600 °C consists primarily of a disordered Si-O structure. It is the product of decomposition and sintering of opaline or hydrous silica that result without melting. Occasionally, a small amount of crystalline impurities may be present, including quartz, cristoballite and or tridymite. When RHA is produced by uncontrolled combustion, the ash is generally crystalline and exhibit poor reactive properties. However, by burning the rice husk under controlled temperature and atmosphere, highly reactive RHA can be obtained [2].

Amorphous silica, is normally extracted from rice husk by acid leaching, and followed by carbon removing process by pyrolisis. Pure silica with a high specific surface area, high melting point and high porosity can be obtained from rice husks. These properties make the ash a valuable raw material for many industries.

1.1.2 The Properties of Rice Husk Ash

Rice husk essentially consists of the following layers, (see Figure 1) (i) outer epidermis coated with a thick cuticle layer of highly silicified sinuous cells, (ii) selerenchyma of hypoderm fibers also with a thick lignified and silicified wall, (iii) spongy parenchyma cells, and (iv) inner epidermis of isodiametric cells [3]. The properties of rice husk ash and its main composition are presented in Table 1[4]. The organic materials consist of cellulose and lignin which turn to CO_2 and CO when rice husk burns in air. The ash contains mainly silica (90%), and a small portion of metal oxides (~ 5%) and residual carbon obtained from open burning.

Table 1: The chemical composition of RHA from reference [4]

Compounds	%
SiO_2	94.04
Al_2O_3	0.249
Fe_2O_3	0.136
CaO	0.622
MgO	0.442
Na_2O	0.023
K_2O	2.49
LOI	3.52
Total	101.5

(LOI: Loss of Ignition)

Rice husk is a highly volatile fuel. The proximate analysis on rice husk samples to determine the weight fractions of volatiles matter, fixed carbon and ash on rice husk were carried out by Mansary and Ghaly [5]. Rice husk samples from four varieties of rice (Lemont, ROK 14, Cp 4 and Pa Potho) were collected for the study. The results of the proximate analysis and chemical composition are given in Table 2 and 3.

Table 2: Analysis of rice husk (% dry basis) [5]

Rice husk	**Volatile matter**	**Fixed carbon**	**Ash**
Lemont	66.40	13.60	20.00
ROK 14	67.30	13.90	18.80
CP 4	63.00	12.40	24.60
Pa Potho	67.60	14.20	18.20
Average	66.08	13.53	20.20

Table 3: Chemical composition of rice husk (% dry basis) [5]

Rice husk	**Cellulose**	**Hemicellulose**	**Lignin**
Lemont	29.20	20.10	30.70
ROK 14	33.47	21.03	26.70
CP 4	25.89	18.10	31.41
Pa Potho	35.50	21.35	24.95
Average	31.02	20.15	28.44

The data colleted from their study shows some sort of similarities in the composition of rice husk. The average of the volatile matter is 66.10 %, 13.53 % for fixed carbon and it contains 20.40 % of ash. Cellulose is the highest component in all the samples with an average percentage of 31.02 %. Based on this table, it shows that ~ 80% is organic material. Therefore rice husk purely contains ~ 20 % of inorganic material which is silica compound.

1.1.3 Production, Purification and Characterization of Silica from Rice Husk Ash

Many studies were carried out to maximize the production, the purification methods and to characterize the surface properties of silica from rice husk ash. In the early 1950's ceramic engineers used RHA as a source of raw material [6]. Ibrahim et.al [7, 8, and 9] had studied the surface properties of silica resulting from thermal treatment of RHA. Silica samples were prepared by burning rice husk ash at various temperatures from 500 °C to 1400 °C for a period of 3 hours. Their findings showed that the ratio of absorbency bands corresponding to the Si---OH and Si---O groups occurring at 810 cm^{-1} gave the amount of Si---OH left undestroyed at each firing temperature.

The results obtained were compared with those of silica gel. Silica gel lost its OH group above 1200 °C while rice husk silica lost it at about 700 °C. No crystalline phase was detected by X-ray diffraction analysis at 700 °C for RHA. It also showed that cristobalite started to appear at 900 °C. The unordered cristobalite phase was found up to 1200 °C. Ordered cristobalite and tridymite were detected by X-ray at 1300 °C and 1400 °C. Ibrahim et.al concluded that rice husk ash silica is similar in nature to silica gel. It follows the sequence of transformation suggested by Florke for the different crystalline